$(C_V, PVT)_X$ PHASE BEHAVIOUR STUDIES ON BINARY MIXTURES HYDROCARBON AND WATER .

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Abstract. The high temperature adiabatic calorimeter-piezometer have been used for experimental investigation of the isochoric heat capacity and pressure-volume- temperature properties of $[xH_2O + (1-x) C_7H_{16}]$ mixtures, containing 0.295 mole fraction of water. The measurements have been carried from 473 K to 553 K along isochores.

1 Introduction

The basic instrument for reception of the information about thermophysical properties of substance in a wide range of parameter (temperatures, pressures and densities) is the equations of state.

Usually, at elaboration of equation of state PVT data are used, and the precision of the worked equation is controlled on calculated on his basis calorical properties, in particular, on the

isochoric heat capacity. As a rule, thermal PVT and calorical C_v properties are studied from different experimental apparatus and different researchers.

The thermal properties are usually studied by various variants of a method of a piezometer. The information about the caloric properties gain in experiments, in which the calorimeters of various constructions are used (Kirillin et al 1963).

At the creation of the equation of state and attempt of results concordance of such disparities investigations take place the serious difficulties. The most complex difficulties appear in near to phase transition fields, where is observed the complex dependence of C_v , PVT properties on temperature. This problem can be decided with the help of the high-temperature adiabatic calorimeter of Amirkhanov.

Design feature of the high-temperature adiabatic calorimeter allow to use it also as a piezometer of constant volume and to receive simultaneously in requirements of the same experiment and same measuring cell the information about the agreement dates about thermal PVT and caloric C_v properties of a studied sample mixture.

The design and development of a calorimeter - piezometer made of stainless steel, was described in detail in a series of earlier papers (Amirkhanov et al 1981; Mirskaya et al 1994).

 Figure 1 shows the automated experimental apparatus schematically.
The realization of experiment is carried out as follows.

Necessary quantity m of a studied mixture relevant to a measured isochore V=const. injected inside previously evacuated of a calorimeter - piezometer (1) through a line (6) of a fine vacuum. After filling by an explored sample, the calorimeter - piezometer is hermetic closed with the help of the specially designed valve (2). After that necessary temperature of experience is get warm with the help of heaters and the thermostat (1). The use of adiabatic semiconductor cover

and automatic high-precision thermoregulators allows thermostatted system with an error which is not excee0ding $\pm 2 \cdot 10^{-5}$ K. After an establishment of a uniform temperature field in a place of an arrangement of a calorimeter - piezometer, measure parameters for calculation of a isochoric heat capacity, according to a relation:

$$C_v = (Q / \Delta T - q_c) / m$$

Where m-mass of studied mixture; Q- heat which has been given to system by a heater, at which temperature of a studied mixture changes on Δ T; q_c - a thermal equivalent of a calorimeter.

The value of q_c was determined in a calibration experiment, in which the fluids (water, n-heptane) were used, for which the precise values of a heat capacity are well known.

The error in determination of an isochoric heat capacity does not exceed 2 %.

For piezometrical measurements a calorimeter with the help of a capillary and specially design need over valve (2) through the differential pressure transducer (3) was connected to system of measuring of pressure. Pressure in a calorimeter - piezometer measure by a compensative method with the help piston gauge (4) and by means of the electrical pressure transducer (5). The differential pressure transducer (3) is used as the zero – device, fixing equality of pressures in a calorimeter - piezometer and a measuring system. The basic part of the differential pressure transducer is the membrane placed between two restrictive surfaces, admitting its travel to both legs from a medial standing on 0.2 mm. It makes of 0.0122% from volume of a calorimeter - piezometer (≈ 420 cm^3 at room temperature). The sensitivity of the zero - device has made 30 Pa. The error of definition of pressure corresponds to a class of precision of the piston gauge and 0.09 % is estimated.

Temperature and pressure effects on the internal volume of calorimeter-piezometer are determined from calculations used the linear expansion coefficients and also from the special experimental procedures.

After realization of a series of measurements transferred to the following point on an isochore, changing temperature.

Examination ($C_{v,x}$, PVT) complex of thermophysical properties of a binary mixture n-heptane, containing 0.295 mole fraction, of water were measured for eight isochores in range of temperatures from 473.15K to 553.15K and densities from 214.20 kg/m^3 to 415.7 kg/m^3.

Studied samples of mixtures prepared from synthetic n-heptane, marks «reference», without supplementary purification and bidistilled of water.

Temperature dependence of the heat capacity $C_{v, x}$ and PVT properties were determined along isochores in the ranges of three-phase equilibria a liquid-liquid-vapour, two-phase and homogeneous, including phase transitions a liquid-liquid and liquid-vapour. The region of examinations including of a critical state of more volatile component - n-heptane, and upper critical temperature of a mixture n-heptane + water.

Components of mixtures {(1-x) C_7H_{16} + xH_2O} are immiscible at room temperature and atmospheric pressure, and the separation interfaces so as between two liquid phases and as vapour phase exist in a wide region of temperatures and pressures.

It was shown feature (Kamilov et al 1996, Mirskaya 1998) behaviour of temperature dependence of a heat capacity on isochores for the water-hydrocarbons mixtures earlier. The breaks of a heat capacity along isochores are observed twice at temperature of liquid-liquid T_{ll} and liquid-vapour T_{lg} phases transitions.

The temperature interval I $T_{ll} - T_{lg}$ I between phase transitions is various for different values of density.

The temperature dependence of the isochoric heat capacity of an investigated mixture n-heptane, containing 0.295 mole fractions of water, is similar of behaviour of function $C_{v,x} = f(T)$ studied before n-heptane mixtures, containing 0.147 and 0.420 moles fractions of water.

The temperature dependence of pressure of a mixture n-heptane, containing 0.295 mole fractions of water is determined on isochores, including of liquid-liquid and liquid-vapour phase transitions.

On isochores the increase of pressure is observed at increase of temperature in three - phase, two - phase and homogeneous states. Change of pressure $(\partial P / \partial T)_{v,x} > 0$ along all measured isochores and also is various for different values of density.

 In the region of densities from 415.6 kg/m^3 to 285.4 kg/m^3 and temperatures up to 508K pressure of a mixture feebly depends on density.

For an investigated mixtures on isochores two fractures are found out during function $P = f(T)$ in points relevant to temperatures of phase transitions liquid -liquid and liquid-vapour.

The isochores are changed slopes $(\partial P / \partial T)_{v,x}$ of at transition of mixtures from three-phase in two-phase and homogeneous phase. The steeper slope of isochores of pressure is observed at higher density of a mixture. The greatest value of $(\partial P / \partial T)_{v,x}$ is observed on isochores at higher densities in a homogeneous state of a mixture.

With decrease of density slopes $(\partial P / \partial T)_{v,x}$ of isochores of pressure decreases in three-phase, two-phase and homogeneous states of mixtures. In the densities 252.3 kg/m^3 $< \rho <$ 214.2 kg/m^3 isochores of pressures are nearly colinearity.

Brunner (1990) has measured P =f(T) dependence for a series of n-alkane+water mixtures by a method of high-pressure optical cell. Results of pressure measuring of n-heptane+water mixtures, submitted in this paper, and dates described by Brunner are in well agreement.

So using the experimental method of high-temperature adiabatic calorimeter-piezometer are received inter coordinated data about PVT properties and isochoric heat capacity. These data will be used for working of the equation of state for n-heptane-water system.

List of symbols.

C_v isochoric heat capacity

X   concentration of water

T   temperature

V   volume

P   pressure

Subscripts:

ll   liquid-liquid phase transition

lg   liquid-vapour phase transition

References

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Figure 1. Schematic view of the experimental apparatus.

     1 calorimeter-piezometer into automatic controlable thermal shields,

     2 over need valve,

     3 differential pressure transducer,

     4 piston gauge

     5 complex in figures for the pressure measurement,

     6 line of fine vacuum and filling of calorimeter-piezometer

Figure 2. $C_{v,x} = f(T)$ dependence for mixture $[(1-x)C_7H_{16} + xH_2O]$, $x = 0.295$ mole fr.

     along isochores with ρ / kg m^3: o - 374.60; ◀ - 258.70.

Figure 3. $P = f(T)$ dependence for mixture $[(1-x)C_7H_{16} + xH_2O]$, $x = 0.295$ mole fr.

     along isochores with ρ / kg m^3:

     ● - 285.4; ◆ - 252.3; ◀ - 230.7; ✿ - 214.2.
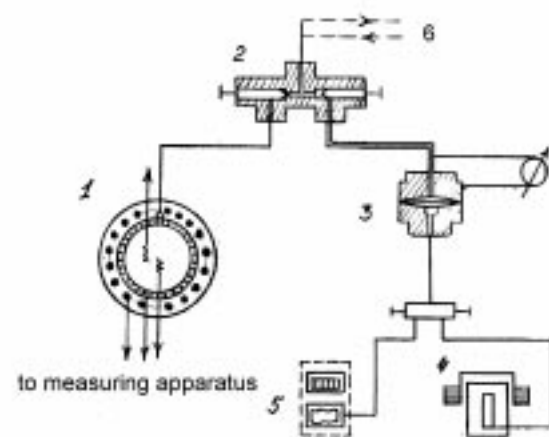
Figure 1
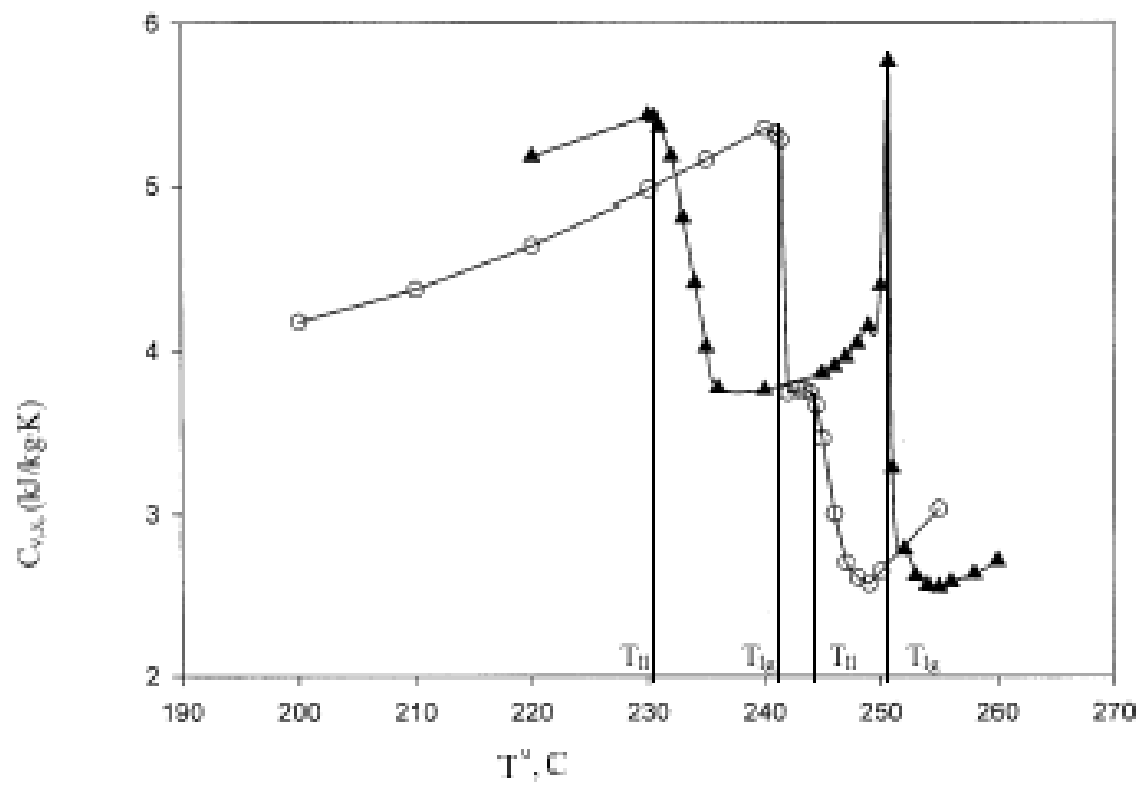
Figure 2.

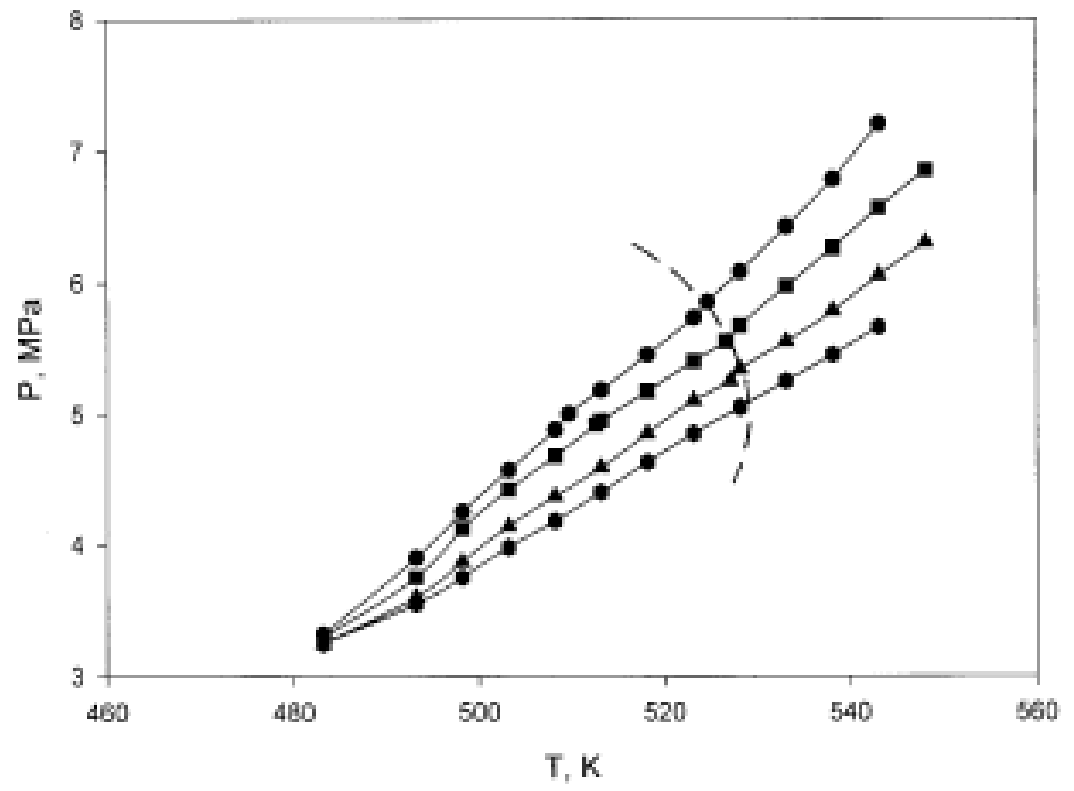Figure 3

Table 1. Experimental values pressure P and temperature T along isochores ρ for

mixture $[(1-x)C_7H_{16} + xH_2O]$, x = 0.295 mole fr.

.T/ K	P/ MPa	T/ K	P/ MPa	T/ K	P/ MPa
$\rho = 214.2$ kg m^{-3}		$\rho = 285.4$ kg m^{-3}		$\rho = 333.4$ kg m^{-3}	
504.57	4.13	514.71	5.39	503.67	4.73
514.57	4.49	516.58	5.52	511.87	5.49
519.51	4.68	519.29	5.64	513.50	5.63
521.66	4.76	522.05	5.79	515.89	5.87
525.86	4.96	524.98	5.87	518.42	6.05
529.73	5.99	528.29	6.11	520.78	6.24
534.31	5.31	532.35	6.38	524.06	6.48
539.28	5.47	538.30	6.77	528.86	6.84
544.22	5.69	524.98	5.87	528.86	6.84
525.86	4.96			533.30	7.23
				538.83	7.75